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Study on Preparation and Photocatalytic Properties of La-Cu_2O/MgO Composites

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Abstract. This paper studied the preparation methods of La-doped Cu_2O/MgO composites. The method used MgO as a carrier, La as a sensitizer and hydrazine hydrate as a reducing agent. The photocatalytic properties of the composite were studied with methyl orange solution as a probe. The La-Cu_2O/MgO composite photocatalyst with the best catalytic effect was prepared in the solution of 50mL 0.1mol/L $Cu(NO_3)_2$ $3H_2O$, adding 10mL 1mol/L NaOH, reaction time 3 hours, hydrazine hydrate dosage 5mL, carrier Magnesium Oxide 1g and lanthanum nitrate doping amount 4%. Under the 40W tungsten filament light, the dosage of La-Cu_2O/MgO composite was 0.2g/50mL, and the degradation rate of methyl orange solution with the concentration of 10mg/L may reach more than 90%.

1. Introduction

Because of its innocuity, low preparation cost and abundant reserves, P type semiconductor Cu_2O which can be excited in the range of visible light is a very promising photocatalytic material [1]. At present, it has been widely used in the photocatalytic degradation of wastewater, the decomposition of water to prepare H_2, solar cells, gas sensors and so on. The theoretical solar utilization rate of Cu_2O is about 14%-20%, but it has been reported to be only 2% [2]. In addition, the photocatalytic effect of Cu_2O is not high, the main reasons are as follows [3]: The first is that the width of the band gap is only about 2.17eV, so the electron hole pair caused by light is very easy to compound; The second is that Cu_2O is instability, which is easier to be oxidized or reduced in the air neutralization liquid phase. In order to solve the above problems, the modification of Cu_2O has become a hot research topic at present [4].

The modification of Cu_2O is mainly aimed at the following three aspects [5]: (1) obtaining a suitable lead/valence band edge potential by modification; (2) increasing the fluidity of the carrier and preventing the recombination of the electron hole pair ; (3)Reducing the photoetching and improving the stability of Cu_2O.

In this paper, MgO is used as a carrier and rare earth La is used as sensitizer to sensitize Cu_2O to form La-doped Cu_2O/MgO composite. The Magnesium Oxide itself is alkaline, so it can avoid interfering with acid catalyst, which can make the composite highly selective. The rare earth ion La^{3+} has good conductivity. In the photocatalytic reaction, it can rapidly transfer the photogenerated electrons on the surface of the Cu_2O. In this way, electron hole separation can be achieved, which can effectively prevent the recombination of electron hole pairs, thereby improving the quantum efficiency of semiconductor and the effective utilization of sunlight in catalytic reaction.

2. Materials and methods

2.1 Materials

Instruments: electronic analytical balance (FA1004 Shanghai Hengping Scientific Instrument Co., Ltd), digital display thermostatic water bath (HH-6 Shanghai Pudong physical optics instrument factory), electric thermostatic drying oven (101 Beijing ever-bright medical instrument factory), X ray diffraction (Rigaku-12KW Japan), tungsten (40W Lianhua Lighting Co., Ltd.) 722s visible spectrophotometer (Shanghai precision scientific instrument Co., Ltd.).

Reagent: Cupric nitrate, sodium hydroxide, hydrazine hydrate (40%), Magnesium Oxide, lanthanum nitrate, hydrogen peroxide (30%), methyl orange, methylene blue, anhydrous ethanol , which was the analytical reagent.

2.2 Preparation of La-Cu_2O/MgO

A molar ratio of lanthanum nitrate and copper nitrate was added to the 50mL solution of 0.1mol/L $Cu(NO_3)_2$ $3H_2O$, then the 1g MgO carrier was impregnated with 24h in the solution. After 24h, a certain volume of 1 mol/L NaOH aqueous solution was quickly added at room temperature. After agitating and aging 10min, a certain volume of 1mol/L hydrazine solution is added by drop by drop to produce red precipitation. After the reaction was completed, the precipitate was washed and filtered, and then was dried in vacuum at 60 3h, then was Shaped-through-pressure. The Shaped precipitate was crushed to 60 to 80 orders, and then the supported Cu_2O catalyst was prepared.

2.3 Characterization of composite materials La-Cu_2O/MgO

The matter phase is analyzed by D/Max-3cX of X-ray powder diffraction (XRD), and IR, and SEM, and UV-visible absorption spectrum etc. The test conditions of XRD: Cu Target k_a line, the Ni filter, the 40kV, 40mA, scanning range 20 °~80 °(2θ), scanning speed 2 °/min using X-ray diffraction.

2.4 Photocatalytic properties of composite materials La-Cu_2O/MgO

40W tungsten lamp was used as a visible light source, and the light distance was 10 cm. The photocatalytic reaction process was: (1) a certain amount of Cu_2O/MgO composite powder was added to the methylene blue solution of 10mg/L;(2) firstly, in the absence of light, the solution was ultrasonic dispersed for 3min and magnetic stirred for 10 min, so that the organic molecular reached adsorption / desorption equilibrium on the catalyst surface; (3) with the light source opening, the photocatalytic reaction was carried out at room temperature, and the suspension system was kept magnetic stirring during the whole process of the photocatalytic reaction; (4) every 20 min beginning the light open, 5 mL suspension sample was removed and centrifuged 10 min, then the upper liquid was absorbed, the solution absorbance of light catalytic was measured with 722S visible spectrophotometer in 665nm.

The degradation rate

$$(\eta) = (A_0\text{-}A_1)/A_0 \times 100\% \quad (1)$$

Type: The A_0 and A_1 was respectively absorbance value of before and after the degradation of methylene blue solution at the maximum absorption wavelength.

3. Results and discussion

3.1 XRD analysis of composite catalyst La-Cu_2O/MgO

The A, B and C in Figure 1 are infrared spectrum of Cu_2O/MgO, 1% La-Cu_2O/MgO and 2% La-Cu_2O/MgO composite by XRD analysis.

Figure 1 show that with the addition increase of rare earth La, the characteristic peak intensity of 35 °- 40 °Cu_2O in each diffraction peak was obviously reduced and the half peak width became larger.

This indicated that the crystallinity of the catalyst decreased, and the broadening of the doping could effectively inhibit the growth of Cu_2O grain, greatly increased the specific surface area of the catalyst, and increased the lattice defect by doping. These all greatly improved the photocatalytic

degradation efficiency of the catalyst [6]. The following degradation experiments also showed that doping could effectively improve the photocatalytic degradation efficiency of the catalyst.

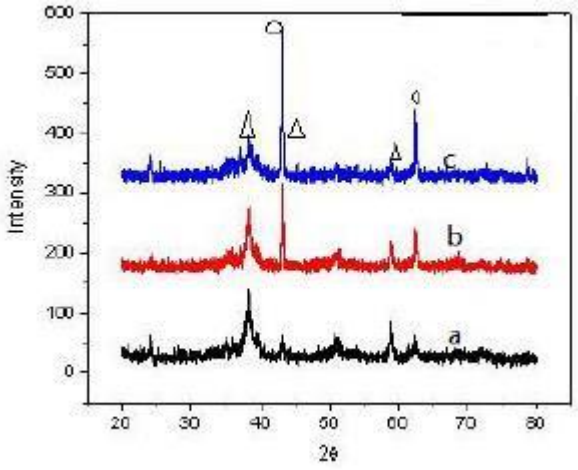

Figure 1. XRD of different doping Cu_2O/MgO a:Cu_2O/MgO; b:1%La-Cu_2O/MgO c:2%La-Cu_2O/MgO (Cu_2O: Δ; MgO: o)

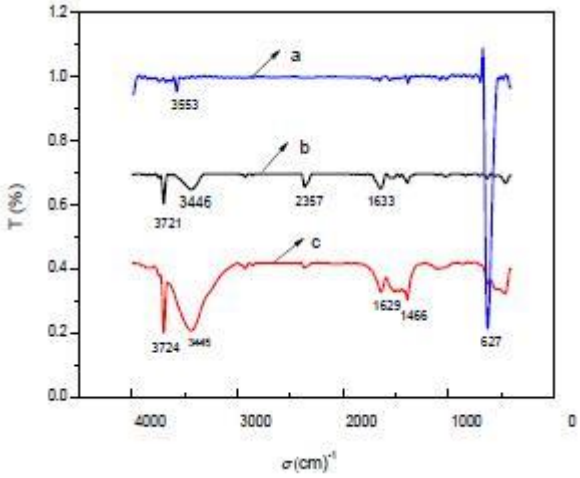

Figure 2. FT-IR images of different doping Cu_2O a:Cu_2O b:Cu_2O/MgO c:2%La-Cu_2O/MgO

3.2 IR analysis of composite catalyst La-Cu_2O/MgO

The A, B and C in Figure 2 are infrared spectrum of Cu_2O, Cu_2O/MgO composite and 2% La-Cu_2O/MgO composite photocatalyst.

Figure 2 shows that the peak spectrum of composite La-doped Cu_2O/MgO and Cu_2O/MgO were basically the same, only varied in strength. The absorption peak at 627cm^{-1} was the Cu-O characteristic stretching vibration peak of cuprous oxide. The absorption peak at 1621-1650 cm^{-1} is the O-H bond stretching vibration peak of the adsorbed water or hydroxyl group. The absorption peak at 3456-3553 cm^{-1} was the hydrogen bond stretching vibration peak of the surface water moleculeor the hydroxyl group. The intensity of absorption peak in the two 2%La-doped samples was very obvious, which was presumed to be caused by the vibration of the adsorbed water. The hydroxyl group and adsorptive water of the catalyst could react with photogenerated holes to form hydroxyl radicals, so the doping of lanthanum played an important role in the photocatalytic reaction.

3.3 SEM analysis of composite catalyst La-Cu_2O/MgO

The Figure 3 shows that the La-doped Cu_2O/MgO composite had better morphology, its particle diameter was evenly distributed, and it was basically spherical. Such morphology could enhance the adsorption of dyes and oxygen molecules by catalysts, and the Cu_2O/MgO heterostructure can accelerate the capture rate of O_2 to photoelectrons, thereby which could improve the electron hole separation efficiency.

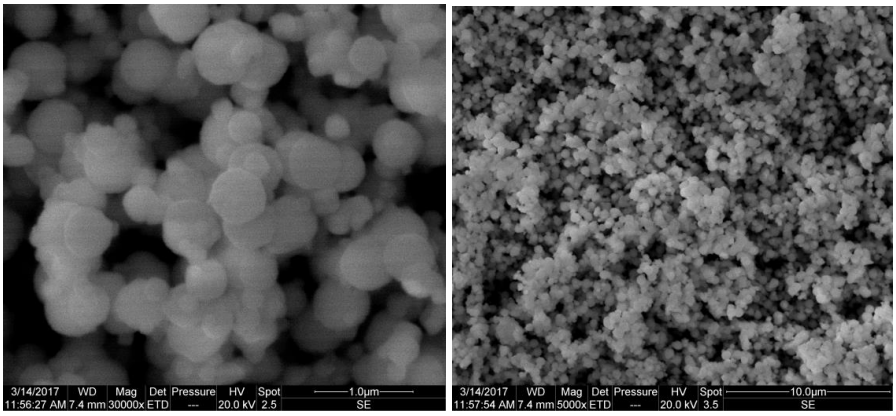

Figure 3. SEM images of La-Cu_2O/MgO

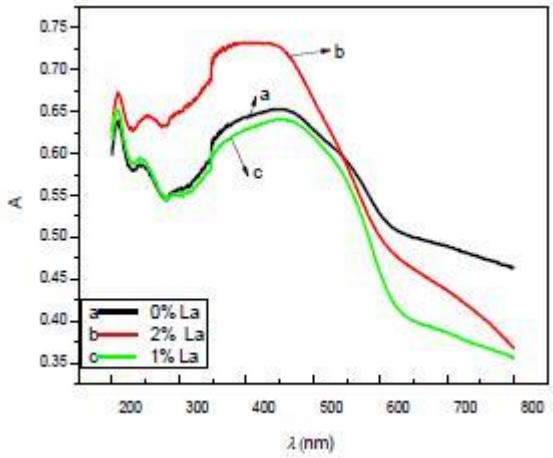

Figure 4. UV-Vis difluse reflectance spectra of pure Cu_2O/MgO and doped Cu_2O/MgO samples

3.4 UV-Vis difluse reflectance spectra of samples

Figure 4 was the UV-visible absorption spectrum of nano Cu_2O/MgO composites, in which the molar ratio of La was respectively 0%, 1%, and 2%.

Figure 4 showed that the photocatalyst doped with 2% La significantly shifted the strongest absorption of light, that was, the absorption light had a blue shift and the absorption strength was increased significantly. It could be seen that in the heterostructure of La-modified Cu_2O/MgO, due to the special 4f electron layer of rare earth ions, Light on the surface of the Cu_2O could cause rapid electron transfer, thus which effectively prevented the electron hole rapid recombination and improved its catalytic stability[7].

At the same time, after the modification of rare earth ions, the surface of the catalyst produced the phenomenon of plasma resonance. This phenomenon would accelerate the production of photoelectron and improve the efficiency of Cu_2O. As shown in Figure 4, the absorption intensity of the two regions of 200nm-230nm and 350nm-450nm after doping La was greatly enhanced.

3.5 Study on photocatalytic properties of La-Cu_2O/MgO

Table 1. Orthogonal experiment table

Experimental number	reaction time A(h)	The amount of NaOH B(mL)	The amount of Hydrazine hydrate C(mL)	The amount of MgO D(g)	Degradation rate(%)
a1	2	5	3	0.5	64.1
a2	2	10	5	1	84.0
a3	2	15	7	1.5	73.9
a4	3	5	5	1.5	77.6
a5	3	10	7	0.5	83.7
a6	3	15	3	1	81.5
a7	4	5	7	1	75.1
a8	4	10	3	1.5	77.4
a9	4	15	5	0.5	82.7
k_1	74.01	72.27	72.67	76.83	
k_2	80.93	80.03	81.43	80.03	
k_3	76.73	79.37	77.57	74.63	
R	6.93	7.77	8.78	5.57	

*3.5.1 Influence of preparation conditions on photocatalytic properties.*Taking methyl orange as the target degrading object and taking degradation rate as evaluation index, the orthogonal method was used to select the best experimental conditions. The detailed experimental design is detailed in the orthogonal experiment Table 1. The effects of the reaction time, the amount of sodium hydroxide, Hydrazine hydrate, and Magnesium Oxide on the catalytic activity of the catalyst were investigated in the table.

According to the results in Table 1, during the preparation of Cu_2O, the four main factors that affect the removal rate of methyl orange were: addition of hydrazine hydrate> addition of NaOH> reaction time > addition of MgO. The best combination of factors was $A_2B_2C_2D_2$. That was to say, the best process conditions for preparing La-Cu_2O/MgO composites by liquid-phase reduction method were as follows: reaction time 3 hours, NaOH 10mL, hydrazine hydrate 5mL, and MgO 1g.

*3.5.2 Effect of addition of La $(NO_3)_3$ on photocatalytic properties.*The effect of different doping amount of La on the catalytic performance of the catalyst was investigated in this experiment. The specific experiments were carried out in the catalytic degradation process in Title 2.4. In the experiment, the amount of catalyst was the same, only the amount of La^{3+} doping in the catalyst was changed. The doping amount of La^{3+} is 0%, 0.5%, 1%, 2%, 4% and 6% respectively. In the experiment, the catalytic effect of pure Cu_2O was also compared. The results of the experiment were shown in Figure5.

As shown in Figure 5, when the molar ratio of La $(NO_3)_3$ was 4%, the photocatalyst had the best photocatalytic effect, which was up to 90%. When the doping amount of La $(NO_3)_3$ kept on increasing, the photocatalytic effect of the catalyst decreased on the contrary. The reason may be, because the atomic radius of La is greater than Cu, when adding a small amount of La, crystal lattice can reduce the volume of the impurities and defects, which was easy to photocatalytic reaction; When the lanthanum was overloaded, the atomic vacancies competition was intensified. In crowded environment, the excited atom needed more energy, and it was also not conducive to the transport of carriers to the interface, thus which inhibited the photocatalytic activity of the catalyst.

*3.5.3 The influence of the amount of catalyst on the photocatalytic performance.*In Figure 6, the effect of the amount of catalyst on the photocatalytic performance was studied. The amount of catalyst added in the experiment was 0.1g, 0.2g, 0.3g, 0.4g, 0.5g.

Figure 6 shows that with the increase of catalyst dosage, the degradation first became larger and then decreased; with the increase of catalyst dosage, the utilization efficiency of photons increased, and the degradation rate increased; when the amount of catalyst was increased to a certain value, the degradation rate would be reduced if the amount of catalyst was increased. This was because when the excess catalyst existed in solution, it would produce interference effects on light, such as shielding, scattering and reflection, which would significantly reduce the photocatalytic efficiency. Therefore, the optimum amount of the catalyst was 0.2g/50mL.

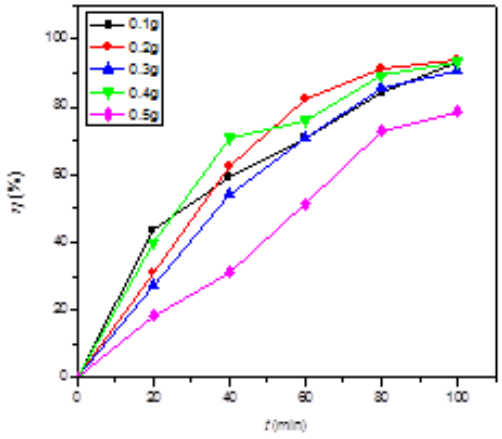

Figure 5. Effect of $La(NO_3)_3$ doping on photocatalytic performance

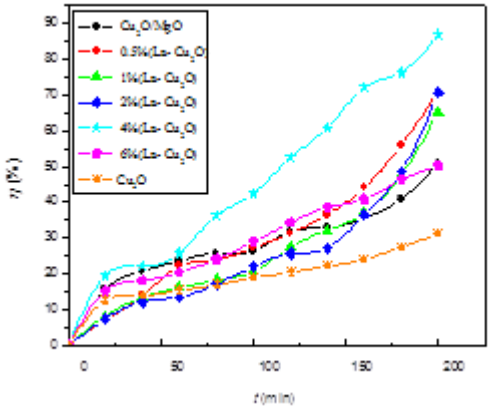

Figure 6. The influence of the amount of catalyst on the photocatalytic performance

4. Conclusions

(1)In this paper, MgO was used as the carrier, rare earth La as sensitizer and hydrazine hydrate as reducing agent to prepare La-doped Cu_2O/MgO composite. With the photocatalytic degradation rate of methyl orange as a probe, the optimum preparation process was determined by the combination of orthogonal experiment and single factor experiment. The best preparation process was: 10mL 1mol/L NaOH was added to 50mL solution of 0.1mol/L $Cu(NO_3)_2$ $3H_2O$, the reaction time was 3 hours, the amount of hydrazine hydrate was 5mL, the amount of Magnesium Oxide added was 1g, and the amount of $La(NO_3)_3$ was 4%.

(2) Characterization of samples by means of IR, UV-Vis, SEM, XRD and other characterization methods, whose results show that the optical absorption of the doped modified composite photocatalyst was obviously shifted to the ultraviolet band, SEM shows that the sample particles are

homogeneous and less agglomeration, and the XRD peak of the modified catalyst is obviously widened.

(3) By studying the photocatalytic active energy of the catalyst, the best catalytic conditions were as follows: incandescent light was 40W, the initial concentration of methyl orange was 10 g/L, the amount of catalyst was 0.2g/50mL, and the activation effect of Cu_2O catalytic activity is best reached more than 90%.

5. Acknowledgement

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6. References

[1] GAO Xin, LIU Xiang-xuan, WANG Xuan-jun, etc. Progress in Research on Cu_2O Photocatalyst, *Journal of Materials Engineering*, Vol. **44** (2016): P.120-128.

[2] Ying Zhang, Bin Deng, Tierui Zhang, etc. Shape Effects of Cu_2O Polyhedral Microcrystals on Photocatalytic Activity, *J. Phys. Chem*. C, Vol.114 (2010): P. 5073-5079.

[3] Zhang Z, Zhong C, Deng Y D, et al. The manufacture of porous cuprous oxide film with photocatalytic properties via an electrochemical-chemical combination method, *RSC Ad-vances*, Vol.**19** (2013): P. 6763-6766.

[4] Sharma P, Sharma S K. Microscopic investigations of Cu_2O nanostructures, *Journal of Alloys and Compounds*, Vol. **557**(2012): P. 152-159.

[5] Tang A, Xiao Y, Ouyang J, Nie S. Preparation, photo-catalytic activity of cuprous oxide nano-crystallites with different sizes. *Alloy. Compd*, Vol. **457** (2008): P. 447 - 451.

[6] Zhang Y.G, Ma L.L, Li J.L, Yu Y. In situ fenton reagent generated fromTiO_2/Cu_2O composite film: a new way to utilize TiO_2 under visible light irradiation. *Environ. Sci. Technol*, Vol. **41** (2007): P. 6264 - 6269.

[7] Xu H,Wang W,Zhu W,Shape evolution and size-controllable synthesis of Cu_2O octahedra and their morphology-dependent photocatalytic properties. *Phys. Chem. B*, Vol.**110** (2006): P. 13829-13834.